

Mass Spectrometric and Quantum Chemical Studies of Gold Speciation in Water Vapor

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The mobility and transport of gold in hydrothermal vapors is strongly influenced by the molecular speciation of gold, which is highly sensitive to pH, oxidation state and water vapor pressure. In this study, electrospray ionization mass spectrometry (ESI-MS) and *ab initio* tools are applied to examine the composition, structure and stability of gold chloride clusters. In brief, electrospray ionization of aqueous AuCl₃ solutions leads to mononuclear clusters of the general form [AuCl₂]⁺(H₂O)_n (*n*=0-4), [AuOHCl]⁺(H₂O)_n (*n*=0-1) and [AuCl₂]⁺(HCl)₂(H₂O)_n (*n*=0-4). Additionally, ion signals due to the dinuclear species [Au₂Cl_{5-x}OH_x]⁺(H₂O)_n (*x*=0-1) are present in mass spectra of electrosprayed aqueous AuCl₃. I also present CCSD(T) level structures and thermodynamic properties of mono- and dinuclear gold clusters, and these data have been applied to examine the role of microsolvation on the stability of individual gold chloride clusters. Results from CCSD(T) calculations indicate that an ion-neutral complex Au⁺(Cl₂)(H₂O)_n, with a formal Au(I) center, is the dominant form of mononuclear gold with *n*=0-2, whereas higher hydrates (*n*>2) are covalently bound [AuCl₂]⁺(H₂O)_n complexes, in which gold exists as Au(III). For dinuclear Au, MP2 calculations show that the lowest energy structure is an ion-molecule cluster [Au₂Cl(Cl₂)₂]⁺ consisting of a single-bridged digold-chloronium ion bound end-on to two dichlorine ligands. The results of this ESI-MS study will allow for a more detailed prediction of gold speciation in low-density aqueous vapors, in particular, in phase-separating hydrothermal fluids. Finally, these ESI-MS studies will also help improve our understanding of Au clustering and aggregation reactions during ore formation processes.